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ORIGINAL ARTICLE

Chemical composition of wet precipitation in ambient environment of Ilorin, north central Nigeria

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Abstract The physico-chemical quality of rainwater in the atmospheric environment of Ilorin in the north central Nigeria has been evaluated. Rainwater samples were collected at every rainy day between March and October 2008. Samples were analysed for pH value, conductivity and water-soluble cations and anions: Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Pb^{2+}, NO_3^-, SO_4^{2-}, PO_4^{3-}, and Cl^-. The average monthly pH ranged between 6.6 and 7.4 with the highest value recorded during the early months of precipitation while the average annual pH value ranged between 6.68 and 7.04. The average annual conductivity ranged between 108.8 μS cm^{-1} and 219.6 μS cm^{-1} with the highest and lowest values recorded at highly urbanized areas and a low density residential area. High levels of Ca^{2+} and NO_3^- ions were observed and together constituted 55% of the total ion mass. Ca^{2+} ion is crustal element and it alone contributed 56% to the total cations while NO_3^- a by-product of atmospheric oxidation of particulate from fossil fuel combustion constituted 53% of total anions measured. Generally speaking, the ionic abundance in precipitation (μg L^{-1}) showed the general trend: $NO_3^- > Cl^- > SO_4^{2-} > PO_4^{3-}$ for anions and $Ca^{2+} > K^+ > Na^+ > Fe^{2+} > Mg^{2+} > Pb^{2+}$ for cations. The average annual SO_4^{2-} concentration ranges between 12.9 and 27.6 μg L^{-1} while the cumulative average for Ilorin was 17.3 μg L^{-1}. The statistical analysis of physico-chemical parameters revealed a strong correlation ($p < 0.01$ and $p < 0.05$) among some sites which was an indication of a common source of inputs of these parameters. Results of the present study suggested that both natural and anthropogenic inputs influence the changes of chemical compositions that occurred during the wet precipitation.

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1. Introduction

The understanding of the chemical composition of the atmospheric aerosols is significant due to its short and long term effects on human health and the ecosystems (Kanellopoulou, 2001; Steinnea, 1990). Automobile, industrial and agrochemical

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particulate emissions are air-borne chemicals and are constantly transported in the air over a long distance from the point of emissions. When it rains, these aerosols come down as chemicals dissolved in the rain (Smirnioudi et al., 1998) and form the damaging constituents of the rain. The presence of heavy metals in the atmosphere is essentially due to the combine effects of waste incineration, fossil fuels and fire-burning. Industrialization, urban growth and low level of hydro-power generation and distribution have led to heavy reliance on fossil fuels (petroleum products and coal) as alternative to power supply. This has caused greater emissions of atmospheric pollutants such as SO_2, NO_x, VOCs and aerosols (Teixiera et al., 2008).

A great percentage of metals as a result of their relative masses, fall through the rain at the place of their production (Nurnberg et al., 1984). But the lighter aerosols, which have a very small falling velocity, are easily transported by the wind and could be deposited through the rain at long distances away from the point of their emissions (Smirnioudi et al., 1998). Therefore, it is expected that the acid components, anions, cations and heavy metals which constitute the chemical components in the rainwater can significantly produce damaging effects on the environment (surface waters, plants, animals and human beings).

The urban areas are more prone to anthropogenic pollution than the rural areas, due to high traffic volume and level of industrialization. Vehicular emission which is due to aging of moving parts, releases heavy metals such as Zn from tyres, Cu from brake linings and Mn from moving parts (Preciado and Li, 2006). Concentrations of industries and industrial processes and mining operations are known to produce the largest emission of As, Cd, Cu, Mn and Zn (Allen et al., 2001). SO_4^{2-}, NO_3^-, PO_4^{3-} are present in the atmosphere partly due to oxidation of SO_2, NO_x from automobile exhaust or mining of phosphate rocks. Atmospheric deposition could be an important source of plant nutrient input to the ecosystem (Kellman et al., 1982).

This paper presents 8 months study of wet precipitation composition carried out on each rainy day in the sites chosen. The average concentrations of the parameters determined were discussed in relation to their environmental fates.

2. Materials and methods

2.1. Study areas

This study was conducted in Ilorin metropolis in the north central region of Nigeria. It is located at latitude 6°29′N and longitude 4°32′E. The climate is characterized by 4–5 months of dry season. The city is located in an agricultural region but fast growing in commercial and industrial activities. Its population was estimated at 1178,420 according to National Population Commission, 2006. The choice of the sampling sites was based on commercial, industrial, traffic volume, or residential lay out. Ten (10) sampling points were selected (Table 1 and Fig. 1) and randomly spaced within the city. The choice was to capture the various anthropogenic activities which may represent the inputs into the precipitation quality of the area.

2.2. Sampling methods

The sampler is made up of a wooden stand of about 6ft tall with an opening at the top that can conveniently hold the 5 L collecting plastic buckets. A small hole was pierced on the bucket lid which was just sufficient to hold in place a large funnel. The containers and funnels were washed with hot soapy water and rinsed several times with deionized water prior to precipitation as a quality control measure. The funnels were covered with sieves to prevent foreign materials and dry precipitation from the collection buckets. The buckets were removed immediately after precipitation and water transferred into a 2.5 L plastic bottles. Hence, the sample collected was wet and not bulk precipitation (Montes and San Jose, 1989).

Field measurement of pH value and electrical conductivity was done immediately after the rain. Samples were colorimetrically analysed for water-soluble macro-nutrients: PO_4-P, NO_3-N, SO_4-S using Spectronic 20. Phosphate determination involved the formation of an antimony–phospho–molybdate complex and an intense blue coloured complex using ascorbic acid (EPA, 1979). Cadmium reduction method was used to convert nitrate to nitrite. The nitrite in the acidic medium reacts with sulphanilic acid to form an amber colour product (Andrew et al., 1975; EPA, 1979). Sulphate was obtained by turbidimetric method involving $BaCl_2$ and colour developed using a conditioning agent (Andrew et al., 1975). Chloride was determined by Volhard method (Andrew et al., 1975). Prior to metal analysis, water samples were acid digested (Adekola et al., 2010). Ca and Mg were obtained by complexometric titration using EDTA, Na and K were determined using flame photometric method while Fe and Pb were determined using Alpha 4 AnalTech Atomic Absorption Spectrometer.

3. Results and discussions

There was variability in the amount of monthly precipitation and consequently the physico-chemical parameters recorded. On the basis of monthly average pH value, site B had the high-

Table 1 Sampling sites' description.

S/No.	Sample label	Site description	Easting's	Northing's
1	A	Eyenkorin Junction	662,780	930,200
2	B	Mandate Housing Estate/Lubcon	665,300	937,240
3	C	Near Gerialimi Roundabout	667,220	935,760
4	D	Ipata Market	671,740	940,000
5	E	Near Maraba Junction	673,180	939,650
6	F	Sango Area	675,540	942,410
7	G	Oloje Housing Estate	665,540	941,540
8	H	University Senior Staff Quarters	678,300	937,540
9	I	Asa Dam Industrial Layout	669,290	934,560
10	J	Taiwo Road/Oko-Erin Junction	670,000	937,900

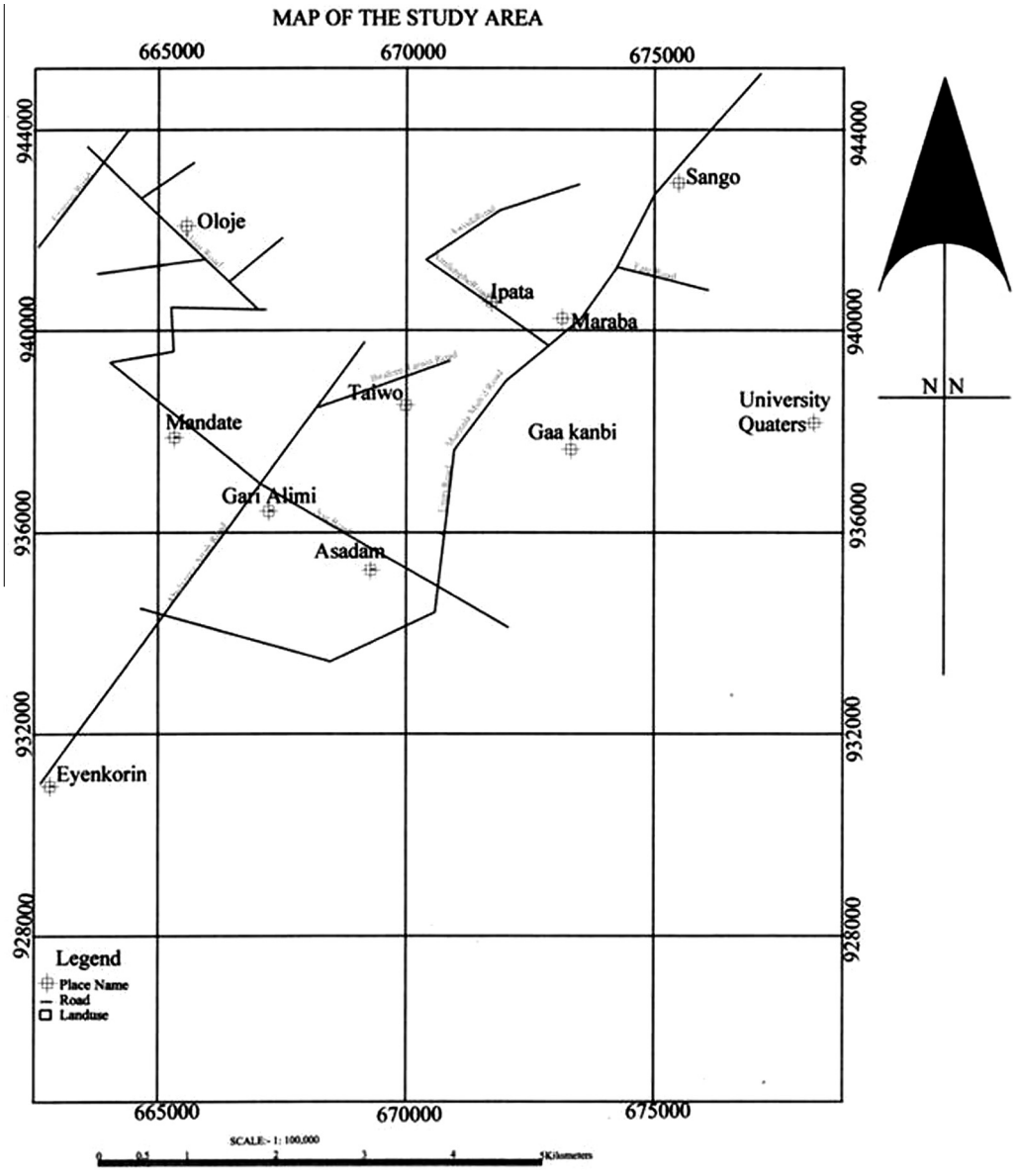

Figure 1 Map of the study areas.

est pH 7.4 for the month of March and the lowest pH 6.6 for site I in the months of May and June (table not shown). However, the average annual pH values ranged between 6.68 and 7.04 across all sites with sites D and G having the highest pH value of 7.04 while site E has the least with average annual value of 6.68 (Table 2 and Fig. 2). This trend can be attributed

Table 2 Annual mean values for pH, conductivity, ions and heavy metals at different sites in Ilorin Metropolis, Ilorin, Kwara State.

Locations	pH	Conductivity ($\mu S\ cm^{-1}$)	Chloride ($\mu g\ L^{-1}$)	Sulphate ($\mu g\ L^{-1}$)	Nitrate ($\mu g\ L^{-1}$)	Phosphate ($\mu g\ L^{-1}$)	Calcium ($\mu g\ L^{-1}$)	Magnesium ($\mu g\ L^{-1}$)	Sodium ($\mu g\ L^{-1}$)	Potassium ($\mu g\ L^{-1}$)	Iron ($\mu g\ L^{-1}$)	Lead ($\mu g\ L^{-1}$)
A	6.97	157.8	36.2	15.7	48.1	7.1	159.5	2.5	17.9	7.7	3.2	
B	6.95	186.9	23.5	16.8	47.4	6.9	49.8	2.7	26.2	12.9	3.5	1.9
C	6.87	219.6	25.0	19.4	61.1	8.0	306.4	3.4	28.7	20.2	2.1	3.5
D	7.07	126.6	21.0	16.0	50.5	8.8	74.1	2.8	23.0	4.7	3.4	
E	6.80	201.6	32.1	15.8	44.5	9.3	280.8	21.8	27.4	5.4	2.7	4.7
F	6.94	117.5	21.7	16.8	48.9	8.6	205.5	15.1	27.4	7.2	2.2	2.1
G	7.04	127.8	24.9	16.2	42.9	7.9	322.1	3.4	21.7	7.5	2.9	5.1
H	6.85	108.8	19.3	12.9	51.1	9.5	100.3	2.2	19.3	7.3	1.7	11.7
I	6.82	172.3	57.6	27.8	46.6	7.8	35.4	3.4	33.1	19.1	4.9	2.4
J	6.68	206.3	31.4	15.6	60.5	8.1	225.6	2.7	22.8	10.8	3.0	

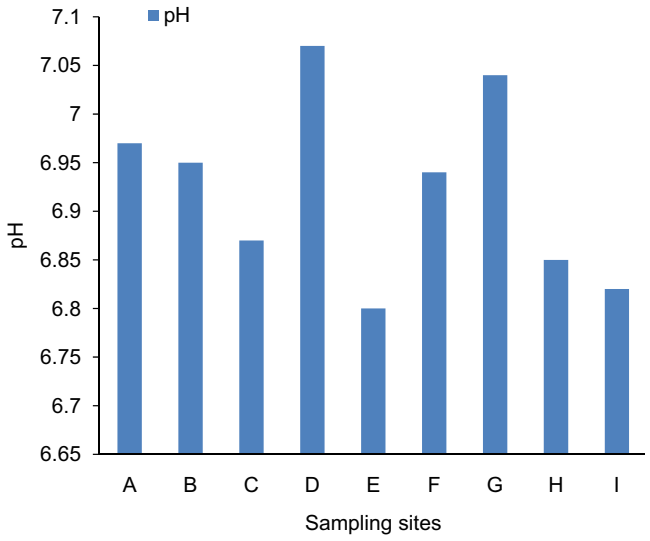

Figure 2 Average annual pH across the sampling sites.

to the fact that sites D and G are heavily populated serving both commercial and residential purposes that are characterized by high pollution, vehicular emissions and activities of electricity power generating sets. The pH values were highest in the first few months of precipitation and this can be observed in the values recorded for March and April (results not shown). The lowest pH value recorded was in June which may be attributed to the low volume of precipitation observed in the previous month of May (42.3 mm). Usually, carbonate buffer as a result of dissolution of CO_2 in rain water accounts for the usual lower pH5.6 (Charlson and Rodhe, 1982). The relatively high annual average pH (6.68–7.04) obtained for these sites was not due to lack of acidity but rather due to neutralization reaction of acidity in precipitation. The acidity in Saharan region is governed by the high content of $CaCO_3$ in the dust as opposed to Europe and North East United States where ammonia is the main neutralizing agent (Al-Momani et al., 2000).

The average monthly conductivity ranged between 35.0 μS cm^{-1} (site F) and 535.0 μS cm^{-1} (site C) for March 2008 and the lowest values were obtained in the months of July and August which correspond to higher precipitation months (318.6 and 226.3 mm, respectively). This observation can partly be adduced to the relatively higher level of dilution of dissolved ions during this period. Comparatively, sites C and H have the highest and lowest average annual conductivities, respectively. This observation may be due to on-going physical construction work at site C while site H is in a remote residential area of the city. Generally speaking, conductivity values were low but the early raining season recorded relatively higher conductivity values than the late wet season due to higher dilution factor (Abegunde and Omisore, 2003). The average annual conductivity (Table 2) ranged between 108.8 and 219.6 μS cm^{-1} with the highest and lowest values at sites H and C, respectively. The average conductivity value in this study is comparable to that obtained in a similar research in Jordan but higher than that of Singapore (Table 3).

The average monthly chloride ion concentrations ranged between 2.0 and 79.3 μg L^{-1} with the highest value recorded at site G for the month of March and lowest for site C. The late wet season had very low values (4.0–15.0 μg L^{-1}) as compared to the early wet season. The average annual chloride concentration ranged between 19.3 μg L^{-1} for site H and 57.6 μg L^{-1} for site I (Table 2). The cumulative average value for Ilorin (Table 3) is relatively lower than the results obtained for cities in some countries such as Jordan, Israel and France (Al-Khashman, 2005; Singer et al., 1993; Al-Momani et al., 1995). A higher chloride and sulphate concentrations indicate the negative impact from the mixture of saline water from the Atlantic Ocean. Therefore, the low concentrations of these ions in wet precipitation in Ilorin probably were due to the near-absence of influence of wind blow from ocean. Chloride dissolution may have contributed to the relatively higher pH value observed during the early precipitation. High chloride

Table 3 The concentrations of major ions in wet precipitation at selected sites of the world. Concentrations are in μg L^{-1}; EC in μS cm^{-1} and pH in pH unit.

Parameters	This study	Petra Region (Jordan)[a]	Carmel (Israel)[b]	Western Med. (France)[c]	Singapore[d]	Guaiba (Brazil)[e]
pH	6.90	6.85		5.39	4.5	5.71
EC	162.5	160.6			31.02	
Cl^-	29.3	80.6	176.3	357.0	22.11	9.18
SO_4^{2-}	17.3	53.2	150.3	42.2	58.71	15.9
NO_3^-	50.2	35.7	28.0	28.0	16.79	2.74
PO_4^{3-}	8.2					
Ca^{2+}	176	163.1	44.7	32.7	21.73	9.83
Mg^{2+}	6.0	62.3	28	35.5	7.46	4.60
Na^+	24.8	75.6	166	261.2	31.08	10.9
K^+	10.3	18.4	3.7	8.5	3.96	3.15
Fe^{2+}	3.0					
Pb^{2+}	3.1					

Key:
[a] Al-Khashman (2005).
[b] Singer et al. (1993).
[c] Al-Momani et al. (1995).
[d] Balasubramanian et al. (2001).
[e] Migliavacca et al. (2005).

concentration may cause early ripening of fruits even before maturity which can probably cause various health hazards especially in animals and humans when consumed. Cadmium was found to be absent in all samples and very few of the samples showed high concentrations for Lead. Also iron was found to have concentrations lower than standards for drinking water recommended by World Health Organization and therefore does not pose any threat to the environment.

The contribution of each ion to the cation/anion ratio and to the total ion mass in precipitation is shown in Fig. 3. The ionic abundance in precipitation ($\mu g\ L^{-1}$) shows the general trend: $NO_3^- > Cl^- > SO_4^{2-} > PO_4^{3-}$ for anions and $Ca^{2+} > K^+ > Na^+ > Fe^{2+} > Mg^{2+} > Pb^{2+}$ for cations. From Fig. 3c, the contributions of the highest and lowest cations (Ca^{2+} and Pb^{2+}) to the total cation mass are 56% and 1%, respectively. The Ca^{2+} ion makes the highest contribution to the total mass of the ions, it accounts for 41% of the total ion mass and Pb^{2+} accounts for 1% of the total ion mass measured (Fig. 3a). The sampling areas were free of any construction activities or other works involving the use of concrete or other forms of Ca except site C where light construction work was on-going. Therefore, the only possible source of Ca^{2+} ion in wet precipitation is through natural source, which are the suspended dust particles. The unusually high concentration of Ca^{2+} ion supports the neutralization mechanism by $CaCO_3$. The contribution of NO_3^- was 14% and 53% to total ion mass and total anions measured, respectively. This highest contribution is due to the atmospheric oxidation of particulates from fossil fuel combustion. The low level of SO_4^{2-} contribution may be due to low level of S in the fossil fuel. The contribution of sea salts (Cl^- and Na^+) to the total ion contents in precipitation was obtained by comparing the mean of the Cl^-/Na^+ molar ratio in rainwater to that of seawater (Samara et al., 1992). Although sea (representing the natural source) is considered the common source of these ions, anthropogenic contribution is not unlikely (Al-Khashman, 2005). The average of Na^+/Cl^- molar ratio was found to be 1.30. A ratio of 0.94 and 1.4 were obtained in Petra and Irbid regions of Jordan, respectively (Al-Khashman, 2005; Al-Momani et al., 2000). A ratio of 1.30 is relatively higher than 0.86 which is

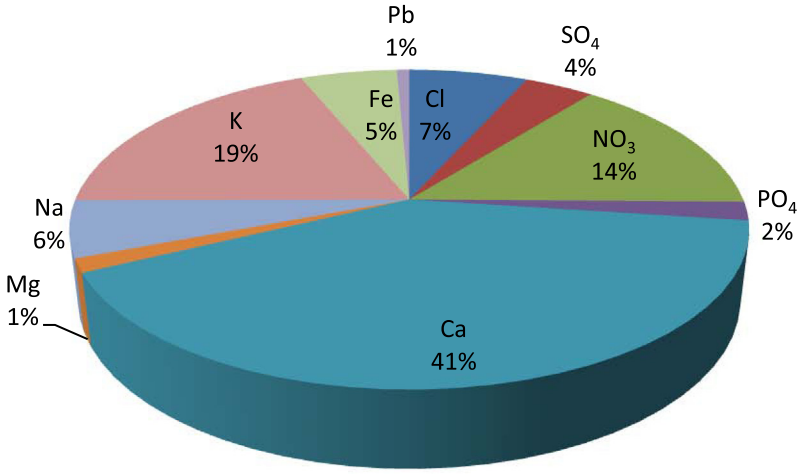

Fig3a: Contribution of ions to the total ion mass

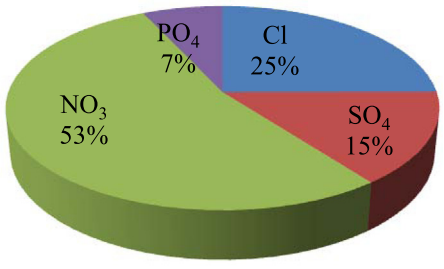

Fig.3b: Contribution of anions to total anion mass

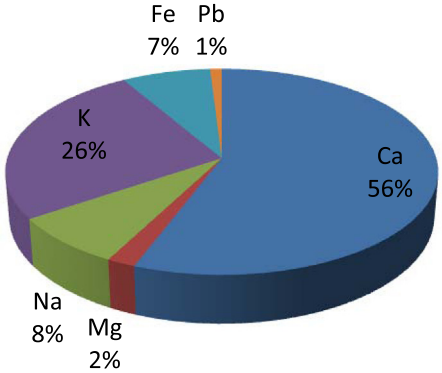

Fig.3c: Contibution of cations to total cation mass

Figure 3 The contribution of each ion to the sum of cations, sum of anions and total ion masses.

the corresponding value for seawater (Al-Khashman, 2005). Therefore, these ions are of natural origin, probably from the suspended dust in the atmosphere.

The average volume weighted concentrations of ions in Ilorin township rainwater for 2008 are presented in Table 3 along side with those reported for representative urban areas around the world. It is observed from the data presented that the concentrations of Ca^{2+} and K^{+} are higher than those reported for Israel, France, Singapore and Brazil except Jordan where both are in the same order of magnitude with our values (Al-Khashman, 2005; Singer et al., 1993; Al-Momani et al., 1995; Balasubramanian et al., 2001; Migliavacca et al., 2005). The higher concentrations are largely due to the Saharan soil dust which contains large fractions of $CaCO_3$. The concentration of marine elements (Mg^{2+}, Na^{+} and Cl^{-}) was relatively lower in this study than those obtained for Jordan, Israel and France (Al-Khashman, 2005; Singer et al., 1993; Al-Momani et al., 1995). The close proximity of sampling sites in these cities as compared to Ilorin, an inter-land city, could be attributed to this difference.

The statistical analysis of the variables is presented in Table 4. The principal component analysis and linear correlation trend of data revealed that there is a strong relationship between various sites as indicated in the values obtained in sites A and E, both sites are characterized by high volume traffic and thus high emissions from motor vehicles. Also sites B

Table 4 Statistical analysis of the variables.

	A	B	C	D	E	F	G	H	I	J
A										
Pearson Correlation	1	−0.19	−0.17	0.489	0.999**	0.517	−0.213	0.518	0.519	0.67
Sig. (2-tailed)		0.652	0.687	0.219	0	0.189	0.613	0.188	0.188	0.069
N	8	8	8	8	8	8	8	8	8	8
B										
Pearson correlation	−0.19	1	0.996**	−0.329	−0.168	0.446	−0.197	0.451	0.452	0.597
Sig. (2-tailed)	0.652		0	0.426	0.691	0.268	0.641	0.262	0.261	0.118
N	8	8	8	8	8	8	8	8	8	8
C										
Pearson correlation	−0.17	0.996**	1	−0.279	−0.148	0.449	−0.234	0.438	0.442	0.609
Sig. (2-tailed)	0.687	0		0.503	0.726	0.264	0.577	0.278	0.273	0.109
N	8	8	8	8	8	8	8	8	8	8
D										
Pearson correlation	0.489	−0.329	−0.279	1	0.477	0.452	0.161	−0.053	−0.041	0.103
Sig. (2-tailed)	0.219	0.426	0.503		0.232	0.26	0.703	0.902	0.924	0.808
N	8	8	8	8	8	8	8	8	8	8
E										
Pearson correlation	0.999**	−0.168	−0.148	0.477	1	0.513	−0.231	0.535	0.535	0.685
Sig. (2-tailed)	0	0.691	0.726	0.232		0.193	0.581	0.172	0.172	0.061
N	8	8	8	8	8	8	8	8	8	8
F										
Pearson correlation	0.517	0.446	0.449	0.452	0.513	1	0.144	0.487	0.479	0.732*
Sig. (2-tailed)	0.189	0.268	0.264	0.26	0.193		0.734	0.221	0.23	0.039
N	8	8	8	8	8	8	8	8	8	8
G										
Pearson correlation	−0.213	−0.197	−0.234	0.161	−0.231	0.144	1	0.131	0.121	−0.329
Sig. (2-tailed)	0.613	0.641	0.577	0.703	0.581	0.734		0.757	0.775	0.427
N	8	8	8	8	8	8	8	8	8	8
H										
Pearson Correlation	0.518	0.451	0.438	−0.053	0.535	0.487	0.131	1	0.999**	0.780*
Sig. (2-tailed)	0.188	0.262	0.278	0.902	0.172	0.221	0.757		0	0.022
N	8	8	8	8	8	8	8	8	8	8
I										
Pearson correlation	0.519	0.452	0.442	−0.041	0.535	0.479	0.121	0.999**	1	0.781*
Sig. (2-tailed)	0.188	0.261	0.273	0.924	0.172	0.23	0.775	0		0.022
N	8	8	8	8	8	8	8	8	8	8
J										
Pearson correlation	0.67	0.597	0.609	0.103	0.685	0.732*	−0.329	0.780*	0.781*	1
Sig. (2-tailed)	0.069	0.118	0.109	0.808	0.061	0.039	0.427	0.022	0.022	
N	8	8	8	8	8	8	8	8	8	8

Key:
* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed);

and C showed a very strong relationship at 99% probability level. These similarities can be attributed to the geography of the area as the distance between sites B and C is less than 3 km. In a similar trend, there also exists a strong relationship between sites H and I which also have a confidence level of 99%. Also using the correlation data obtained, there is a relationship between samples from sites J and F, H and I as shown in Table 4 with a p value of less than 95%. The correlations at 95% confidence level for these sites suggest common inputs of parameters considered in this study.

4. Conclusion

The chemistry and chemical composition of wet precipitation in Ilorin, a city in the middle belt of Nigeria have been investigated and compared with similar works around the globe. The values of pH, electrical conductivity (EC) and Ca^{2+} ion were close to those reported for southern and Northern Jordan. The average annual pH value was about neutral (6.68–7.04). The pH values were highest in the first few months of precipitation (March and April) and lowest at the peak of the rain due to dilution factor. The neutrality of the precipitation underscores the low level of industrial and vehicular activities in Ilorin. The unusual high mean concentration of Ca^{2+} was attributed mainly to the composition of Saharan dust soil. Na^{+} and Cl^{-} concentrations were due to the influence of natural source rather than anthropogenic source. Our results suggested that neutralization mechanism was due to carbonization from Saharan dust.

Statistical analysis including linear correlation trend of data revealed that there is a strong relationship between various sites in terms of variables analysed. This suggests a common source of inputs, mainly from natural source into the precipitation. In summary, the chemistry of wet precipitation in Ilorin is greatly influenced by both natural and anthropogenic sources.

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